Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.102$
$S = 0.956$
5045 reflections
300 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.198$ e Å^{-3}
$\Delta\rho_{\min} = -0.297$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S1—C11	1.782 (2)	N31—C36	1.338 (2)
S1—C21	1.783 (2)	N41—C42	1.342 (2)
O14—C14	1.363 (2)	N41—C46	1.339 (2)
O24—C24	1.354 (2)	N51—C52	1.340 (2)
N31—C32	1.333 (2)	N51—C56	1.339 (2)
C11—S1—C21	102.38 (7)	O24—C24—C23	122.8 (2)
O14—C14—C13	117.7 (1)	C32—N31—C36	116.0 (2)
O14—C14—C15	122.7 (1)	C42—N41—C46	116.7 (2)
O24—C24—C25	117.9 (1)	C52—N51—C56	115.7 (2)
C21—S1—C11—C12	−57.2 (2)	C11—S1—C21—C22	−90.0 (1)
C21—S1—C11—C16	125.3 (1)	C11—S1—C21—C26	92.6 (1)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O14—H14···N31	0.84	1.92	2.736 (2)	162
O24—H24···N41	0.84	1.85	2.683 (2)	169

Compound (I) crystallized in the monoclinic system; space group $P2_1/c$ from the systematic absences. H atoms were treated as riding atoms with C—H = 0.95 and O—H = 0.84 Å.

Data collection: *KappaCCD Server Software* (Nonius, 1997). Cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997). Data reduction: *DENZO-SMN*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

X-ray data were collected at the University of Toronto using a Nonius KappaCCD diffractometer purchased with funds from NSERC Canada. RMG thanks EPSRC (UK) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1306). Services for accessing these data are described at the back of the journal.

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Self-templating of large rings by small rings in 4,4′-bipyridyl–3,4-dihydroxy-3-cyclobutene-1,2-dione (2/3)

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Abstract

The title compound is a salt, bis(4,4′-bipyridyl-4,4′-diium) bis[3,4-dihydroxy-3-cyclobutene-1,2-dionate(1−)] 3,4-dihydroxy-3-cyclobutene-1,2-dionate(2−), $2C_{10}H_{10}N_2^{2+}\cdot 2C_4HO_4^{-}\cdot C_4O_4^{2-}$. The cations and the $(C_4O_4)^{2-}$ anions are linked by two types of short N—H···O hydrogen bond [N···O 2.595 (2) and 2.622 (2) Å; N—H···O 167 and 170°] to form a planar rectangular net built from a single type of centrosymmetric $R^6_8(56)$ ring. The $(C_4HO_4)^{-}$ anions are linked by paired short O—H···O hydrogen bonds [O···O 2.471 (2) Å and O—H···O 152°] into centrosymmetric dimers containing an

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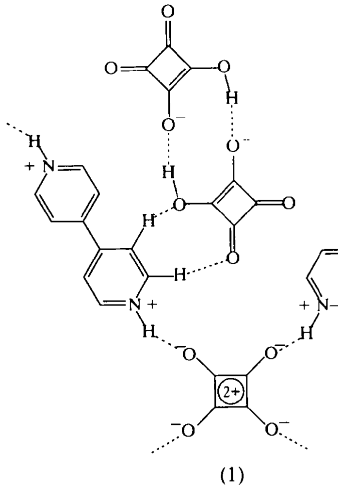
$R_2^2(10)$ motif. A $[(C_4HO_4)^-]_2$ dimer lies at the centre of each $R_8^6(56)$ ring, and is linked to it by two C—H···O hydrogen bonds [C···O 3.318 (3) and 3.165 (3) Å; C—H···O 155 and 151°].

Comment

3,4-Dihydroxy-3-cyclobutenedione (squaric acid), $C_4H_2O_4$, is a strong dibasic acid whose p*K* values have been reported as 1.7 and 3.2 (Ireland & Walton, 1967), and as 1.2 (2) and 3.48 (2) (MacDonald, 1968). It can thus readily form both the monoanion $(C_4HO_4)^-$ and the square-planar dianion $(C_4O_4)^{2-}$, and is thus a versatile building unit for supramolecular chemistry; the dianion in particular may be expected to function as a strong hydrogen-bond acceptor with a structurally well defined array of acceptor sites (Karle *et al.*, 1996). In combination with 4,4′-bipyridyl, squaric acid has been observed to form the 1:1 salt $(C_{10}H_9N_2)^+\cdot(C_4HO_4)^-$, in which the ions are linked into chains of alternating cations and anions by means of O—H···N and N—H···O hydrogen bonds (Reetz *et al.*, 1994). We have now found a second adduct, (1), formed by these two molecular components, of 2:3 stoichiometry, *i.e.* $2C_{10}H_8N_3\cdot3C_4H_2O_4$, which proves to be the salt $2(C_{10}H_{10}N_2)^{2+}\cdot2(C_4HO_4)^-\cdot(C_4O_4)^{2-}$, containing both $(C_4HO_4)^-$ and $(C_4O_4)^{2-}$ anions, and exhibiting a self-templating effect in that dimeric units of the monoanion are enclosed within the large rings of a two-dimensional network built from cations and dianions.



(1)

The asymmetric unit of (1) (Fig. 1) contains a squarate $(C_4O_4)^{2-}$ dianion, lying across a centre of inversion, and a $(C_4HO_4)^-$ monoanion and a bipyridyl $(HNC_5H_4\text{–}C_5H_4NH)^{2+}$ dication, both lying in general positions; hence, there are 1.5 squarate units per bipyridyl, consistent with the 2:3 stoichiometry deduced from microanalytical data. The monoanions are linked into centrosymmetric cyclic dimers by means of O—H···O hydrogen bonds, forming an $R_2^2(10)$ motif (Fig. 2), and the dianions and cations are linked by means of two independent N—H···O hydrogen bonds (Table 2) into continuous two-dimensional nets built from a single type of $R_8^6(56)$ ring (Fig. 2). Normally rings of this size lead to extensive interweaving (Batten & Robson, 1998; Ferguson *et al.*, 1998); the effective area of the $R_8^6(56)$ rings in (1), taking due account of the van der Waals surfaces of all the constituent components, is *ca* 110 Å^2, and thus one or more strands from other nets might well be able to pass through such a ring (Ferguson *et al.*, 1998). However, the centre of each $R_8^6(56)$ ring within the nearly planar net is, in fact, occupied by one of the $[(C_4HO_4)^-]_2$ units; each dimer unit is linked to the surrounding large ring by four C—H···O hydrogen bonds (Fig. 2). The presence of this dimer unit prevents both the occurrence of interweaving and also the collapse of the two-dimensional net into an alternative conformation with a much smaller area within the rings. In effect, the $R_2^2(10)$ dimer acts as a template for the formation of the surrounding $R_8^6(56)$ rings, and the whole structure-forming process may be regarded as an example of self-templating, in which one of the molecular building blocks acts not only as a component of the large ring, but also as the template for its formation.

The squarate dianion was placed, for convenience, across the centre of inversion at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; other such anions are thus found at each of the unit-cell vertices. The large rings forming the two-dimensional nets (Fig. 2) are built from just two types of hard hydrogen bond (Table 2); N11 acts as hydrogen-bond donor to O1 within the asymmetric unit (Fig. 1), and N21 at (*x*, *y*, *z*) acts as donor to O2 at $(-\frac{1}{2}-x, -\frac{1}{2}+y, \frac{3}{2}-z)$. Propagation of these two interactions by the space group serves

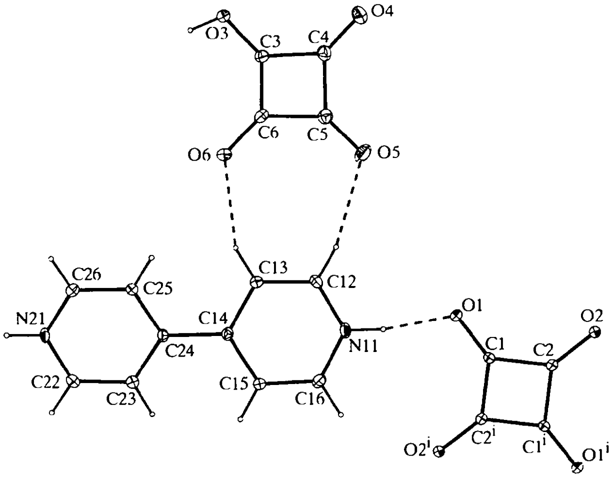


Fig. 1. The asymmetric unit of (1) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1-x, 1-y, 1-z$.]

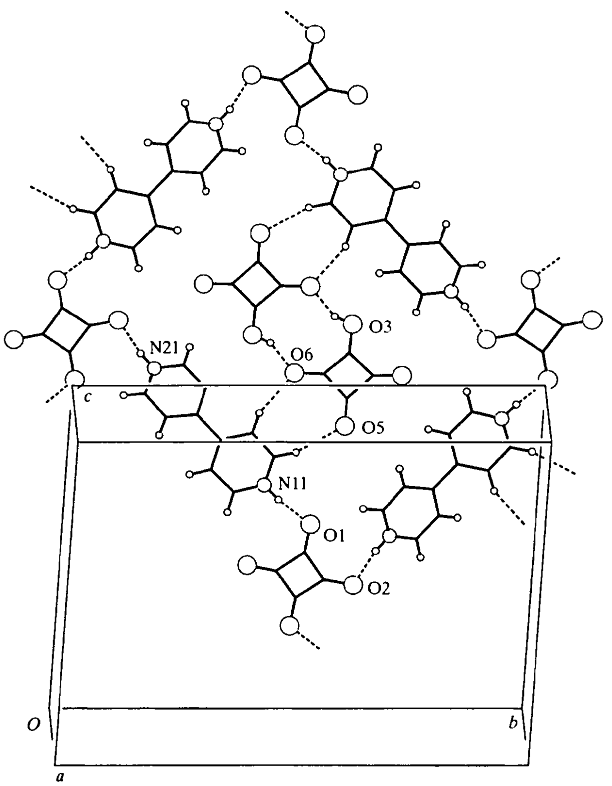


Fig. 2. Part of the crystal structure of (1), showing the $[(C_4HO_4)^-]_2$ dimer unit within one of the $R_8^6(56)$ rings of the (103) net.

to link the dianion centred at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ to four others centred at $(-1,0,1)$, $(-1,1,1)$, $(2,0,0)$ and $(2,1,0)$, with, in each case, a linker consisting of just one bipyridyl cation. The net thus formed can therefore be regarded as built from zigzag $C_2^2(14)$ chains running parallel to [010] and generated by the 2_1 axes, and similar $C_2^2(14)$ chains running parallel to $[30\bar{1}]$ generated by the glide planes. The rectangular net thus formed lies parallel to (103). An alternative description is in terms of the shape and connectivity of the components (Stang & Olenyuk, 1997); the cations are linear building blocks with two donor sites, denoted L^2, and the squarate dianions are angular components with four acceptor sites, A^4, so that the supramolecular architecture may be summarized in terms of the components of a single $R_8^6(56)$ ring as $A_2^4L_4^2$.

Within the internal dimer, centred at $(-1,\frac{1}{2},1)$, O3 at (x, y, z) acts as hydrogen-bond donor towards O6 at $(-2-x, 1-y, 2-z)$, with a very short O···O distance (Table 2); careful examination of difference maps showed that H3 is bonded unambiguously to O3, rather than being symmetrically disposed between the two O atoms. The dimer units are connected to the (103) nets by pairs of C—H···O hydrogen bonds; C12 and C13 act as donors to O5 and O6, respectively, within the asymmetric unit, so that each centrosymmetric $[(C_4HO_4)^-]_2$ unit forms four such bonds to the same net. Of these two hydrogen bonds, that involving C13 and O6 has the smaller H···O and C···O distances (Table 2), and is thus probably the more important. Space-filling plots demonstrate the almost perfect fit of these dimers to the rectangular reticulations in the (103) net, and examination of the structure with *PLATON* (Spek, 1999) showed that there were no solvent-accessible voids in the crystal lattice.

There are no hard hydrogen bonds linking the near planar (103) nets, but soft C—H···O hydrogen bonds provide weak links. The C25 atom of the cation at (x, y, z) acts as a hydrogen-bond donor to O3 in the monoanion at $(-1-x, 1-y, 2-z)$, which is a component of the adjacent net in the [100] direction; the symmetry-related C25 atom at $(1-x, 1-y, 1-z)$ similarly provides a link to the adjacent net in the $[\bar{1}00]$ direction. Hence, each (103) net is linked to the two neighbouring nets. Surprisingly, there are no $\pi\cdots\pi$ stacking interactions involving the bipyridyl units.

The $(C_4O_4)^{2-}$ dianion shows strong evidence of π-electron delocalization, and exhibits almost perfect D_{4h} (4/*mmm*) molecular symmetry (Table 1); the C—O distances are very similar both to the mean value (1.255 Å) of 70 such bonds recorded in the Cambridge Structural Database (CSD; Allen & Kennard, 1993) and to the mean value (1.251 Å) found in oxalate ions $(C_2O_4)^{2-}$, while the C—C distances are similar to the mean value (1.455 Å) for the central C—C bond in conjugated dienes (Allen *et al.*, 1987). On the other hand, the $(C_4HO_4)^-$ monoanion shows very strong bond fixation (Table 1) with little evidence for any delocalization beyond the hetero-allylic enolate portion; in particular, the dimensions of the O4—C4—C5—O5 fragment are similar to those found in 1,2-diketones (Ferguson *et al.*, 1996; Glidewell *et al.*, 1996, 1997), and the C—O(H) distance is comparable to the mean (1.307 Å) of the values recorded in the CSD. The bond lengths in the cation are typical of their types, but the C—N—C angles are both significantly larger than 120°; in unprotonated bipyridyls, this angle is typically well below 120°. The dihedral angle between the the two ring planes in the cation is 18.8 (1)°.

The preference for layer motifs in self-assembled solids containing $(C_4O_4)^{2-}$ and/or $(C_4HO_4)^-$ has been noted previously (Karle *et al.*, 1996). The unusual feature in the structure of (1) is the lack of participation in hard hydrogen bonds of two of the O atoms (O4 and O5) in the monoanion; this is a consequence of the very large excess of hard acceptors over hard donors, only partially relieved by the formation of soft C—H···O hydrogen bonds (Table 2).

Experimental

Stoichiometric quantities of the two neutral components were dissolved separately in methanol. These solutions were mixed and the resulting solution set aside to crystallize, providing very thin analytically pure orange plates of (1). Analysis, found: C 58.6, H 3.2, N 8.7%; $C_{32}H_{22}N_4O_{12}$ requires: C 58.7, H 3.4, N 8.6%. Crystals suitable for single-crystal X-ray diffraction were selected directly from the analytical sample.

Crystal data

$2C_{10}H_{10}N_2^{2+}\cdot 2C_4HO_4^{-}\cdot C_4O_4^{2-}$
$M_r = 654.54$
Monoclinic
$P2_1/n$
$a = 3.7335\,(7)$ Å
$b = 20.116\,(4)$ Å
$c = 18.033\,(4)$ Å
$\beta = 91.708\,(5)°$
$V = 1353.7\,(5)$ Å^3
$Z = 2$
$D_x = 1.606$ Mg m^{-3}
D_m not measured

Synchrotron radiation
$\lambda = 0.68910$ Å
Cell parameters from 2993 reflections
$\theta = 3.44$–$28.95°$
$\mu = 0.126$ mm^{-1}
$T = 150\,(2)$ K
Plate
0.05 × 0.05 × 0.01 mm
Orange

Data collection

Siemens SMART CCD diffractometer
ω rotation with narrow frames
Absorption correction: none
9562 measured reflections
3783 independent reflections

2071 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.072$
$\theta_{\rm max} = 29.48°$
$h = -5 \rightarrow 3$
$k = -28 \rightarrow 23$
$l = -24 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.144$
$S = 0.894$
3783 reflections
219 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0740P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.342$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.301$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997*a*)
Extinction coefficient: 0.019 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C1	1.257 (3)	O3—C3	1.307 (3)
O2—C2	1.255 (3)	O4—C4	1.227 (3)
C1—C2	1.455 (3)	O5—C5	1.226 (3)
C1—C2$^{\rm i}$	1.458 (3)	O6—C6	1.258 (3)
N11—C12	1.339 (3)	C3—C4	1.449 (3)
N11—C16	1.341 (3)	C3—C6	1.416 (3)
N21—C22	1.341 (3)	C4—C5	1.501 (3)
N21—C26	1.333 (3)	C5—C6	1.486 (3)
O1—C1—C2	134.5 (2)	C6—C3—C4	93.4 (2)
O1—C1—C2$^{\rm i}$	135.3 (2)	O4—C4—C3	135.5 (2)
C2—C1—C2$^{\rm i}$	90.2 (2)	O4—C4—C5	136.4 (2)
O2—C2—C1	135.3 (2)	C3—C4—C5	88.1 (2)
O2—C2—C1$^{\rm i}$	134.9 (2)	O5—C5—C6	135.5 (2)
C1—C2—C1$^{\rm i}$	89.8 (2)	O5—C5—C4	136.0 (2)
C12—N11—C16	121.9 (2)	C6—C5—C4	88.5 (2)
C26—N21—C22	122.1 (2)	O6—C6—C3	137.0 (2)
O3—C3—C6	136.5 (2)	O6—C6—C5	133.1 (2)
O3—C3—C4	130.2 (2)	C3—C6—C5	90.0 (2)
C23—C24—C14—C13	160.2 (2)	C23—C24—C14—C15	−18.8 (3)
C25—C24—C14—C13	−18.7 (3)	C25—C24—C14—C15	162.3 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O6$^{\rm i}$	0.84	1.70	2.471 (2)	152
N11—H11···O1	0.88	1.73	2.595 (2)	167
N21—H21···O2$^{\rm ii}$	0.88	1.75	2.622 (2)	170
C12—H12···O5	0.95	2.43	3.318 (3)	155
C13—H13···O6	0.95	2.30	3.165 (3)	151
C25—H25···O3$^{\rm iii}$	0.95	2.41	3.235 (3)	145

Symmetry codes: (i) $-2 - x, 1 - y, 2 - z$; (ii) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $-1 - x, 1 - y, 2 - z$.

Compound (1) crystallized in the monoclinic system; space group $P2_1/n$ from the systematic absences. H atoms were treated as riding atoms with C—H = 0.95, N—H = 0.88 and O—H = 0.84 Å.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1996). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*b*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1999). Software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

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Acta Cryst. (1999). C55, 1896–1899

A three-dimensional hydrogen-bonded framework in piperazine–3,4-dihydroxy-3-cyclobutene-1,2-dione–water (1/1/2)

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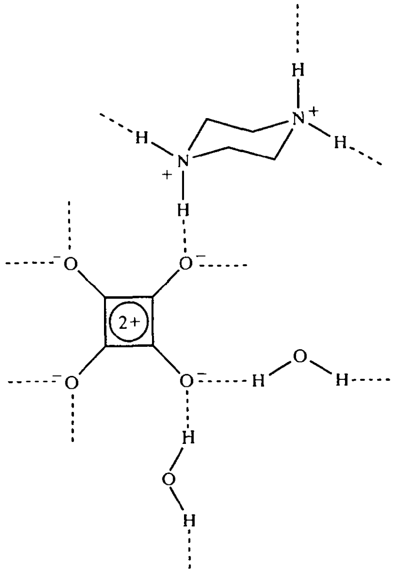
Abstract

The title compound, piperazine-1,4-diium 3,4-dihydroxy-3-cyclobutene-1,2-dionate(2−) dihydrate, is a hydrated salt, $C_4H_{12}N_2^{2+}\cdot C_4O_4^{2-}\cdot 2H_2O$. The water molecules and the centrosymmetric anions are linked by O—H···O hydrogen bonds into two-dimensional nets built from a single type of $R_8^6(24)$ ring. Adjacent nets are linked by the centrosymmetric cations, each of which forms four N—H···O hydrogen bonds, with four different anions as acceptors.

Comment

The dianion $(C_4O_4)^{2-}$ is readily formed from squaric acid (3,4-dihydroxy-3-butenedione, $C_4H_2O_4$) in the presence or organic bases such as amines and in such circumstances it can act as a powerful acceptor of hydrogen bonds, imparting a strong bias towards the formation of planar two-dimensional supramolecular structures (Karle *et al.*, 1996). Piperazine, $HN(CH_2CH_2)_2NH$, is a strongly basic amine which readily forms the $[H_2N(CH_2CH_2)_2NH_2]^{2+}$ dication, where all four N—H bonds, which lie in a common plane, are generally active in hydrogen-bond formation (Coupar *et al.*, 1996; Ferguson *et al.*, 1998). The combination of these two ions might therefore be reasonably expected to give rise to a planar supramolecular system.

Cocrystallization of piperazine and squaric acid from organic solvents such as light alcohols, acetone or tetrahydrofuran gave extremely rapid precipitation of very tiny crystals wholly unsuitable for single-crystal X-ray diffraction, presumably because of the rather low solubility of the ionic product in these solvents. Cocrystallization from water, however, provided excellent crystals of the dihydrate, $(C_4H_{12}N_4)^{2+}\cdot(C_4O_4)^{2-}\cdot 2H_2O$, (1), whose structure is reported here.



(1)

The molecular structure of the asymmetric unit of (1) is shown in Fig. 1. Compound (1) has a three-dimensional framework structure but, as in previously reported examples of three-dimensional organic salts (Glidewell *et al.*, 1999; Gregson *et al.*, 1999), it is possible to identify a substructure of lower dimensionality built from a subset of the molecular building blocks. In compound (1), it is possible to identify two-dimensional nets (Fig. 2) built from just the anions and the water molecules, and the overall structure of (1) is most conveniently described in terms of firstly these nets and secondly the linking of these nets by the cations (Fig. 3), so forming the three-dimensional framework. The two-dimensional net can itself be most simply analysed in terms of a one-dimensional chain motif (Fig. 2).

The $(C_4H_{12}N_2)^{2+}$ cation and the $(C_4O_4)^{2-}$ anion both lie across centres of inversion, and the asymmetric unit (Fig. 1) consists of one half of each of these ions, together with a water molecule lying in a general position. The anion was placed across the inversion centre at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ and hence, with the asymmetric unit selected, the cation is centred at $(0,1,\frac{1}{2})$. The cation

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